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Unsymmetric Electronic Push−Pull Bipyrroles − Synthesis, Spectroelectrochemical, and Photophysical Investigation

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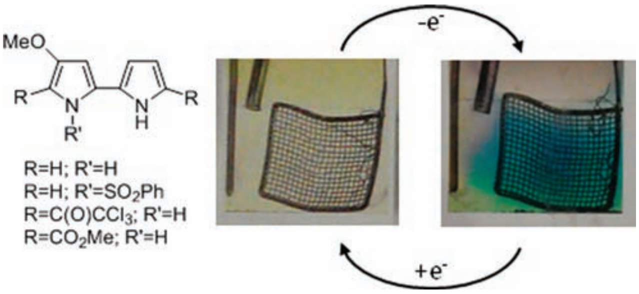

The electrochromic and photophysical behaviors of unsymmetric bipyrroles were observed as intense color changes of the oxidized products relative to the neutral form. The color of the oxidized form and the oxidation potential were both tunable contingent on electronic group and substitution.

Heterocycles play major roles in plastic electronics due in part to their capacity to be polymerized into functional materials with low oxidation potentials and stable radical ionic intermediates. Thiophenes such as EDOT (**5**) have been widely used because of their electronic and conductive properties.[1,2] The stability of their electrochemically induced polarons and bipolarons accompanied by significant color changes in the visible region have led to their use as displays in consumer electronics including tinted windows, goggles, and personal portable devices.[3−5]

Demands on device performance for increased fast switching times and electrochromic materials capable of producing a gamut of colors have driven the search for new heterocycle comonomers to improve performance and expand the color palette. Comonomers have typically consisted of dyads and triads containing electron-rich and -deficient aryl groups sandwiched between polymerizable end groups, such as EDOT.[2,6] Although color and oxidation potential may be tuned by incorporating such electron donor and acceptor units, the overall properties of such devices remain typically governed by the terminal EDOT moieties.[7]

Pyrroles represent viable alternatives for addressing challenges in organic electronics. Although they possess low oxidation potentials similar to their thiophene analogues, pyrroles may exhibit different spectroscopic and photophysical properties due to the nitrogen heteroatom.[8,9] The nitrogen in the heterocycle contributes to decreasing the oxidation potential (E_{pa}) as seen with the E_{pa} of 2,2′-bipyrrole, which is 650 mV lower than the corresponding bithiophene.[10] One advantage of pyrroles is their higher HOMO−LUMO energy gaps relative to their thiophene counterparts. In spite of their properties, pyrroles have been less widely used than thiophenes in functional materials and devices.[11]

In the context of a program on comonomer research,[12−15] we have been investigating pyrrole derivatives to characterize their oxidation potential for potential use in tunable spectroelectrochemical color devices. Unsymmetric bipyrroles have been targeted to examine substituent effects on electrochromic behavior. The bipyrroles **1**−**4** (Chart 1) were synthesized and their structure−property relationships characterized spectroscopically, electrochemically, and spectroelectrochemically. These compounds may be ideal electrochromes because their anodically induced intermediates and significant color changes can be produced at low potentials. Structure−property relationships have been studied to determine the effect of the electron-donating methoxy and different electron-withdrawing groups (trichloromethyl ketone, ester, and sulfonamide) on the oxidation potentials and spectroscopic properties of the neutral and radical cation species.

Synthesis

2,2-Bipyrrole[16] has served as a precursor for synthesis of prodigiosin natural products,[17] expanded porphyrins,[18−20]

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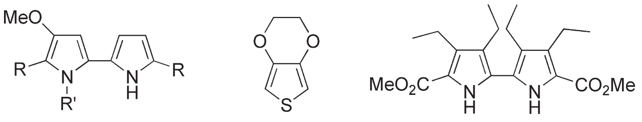
CHART 1. **Bipyrroles Prepared and Investigated and Representative Analogue**



1 R=H; R'=H
2 R=H; R'=SO$_2$Ph
3 R=C(O)CCl$_3$; R'=H
4 R=CO$_2$Me; R'=H

5

6

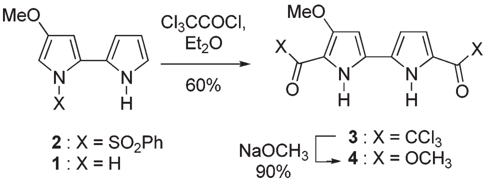
and conducting polymers with nanofiber morphology.[21] Oxidative couplings of 1,1′-carbonyldipyrroles,[22] 2-trimethylstannylated pyrroles,[23] and pyrrole,[24] dehalogen coupling of halogenated pyrroles, and desulfurization of thienodipyrroles[25] all have been used to assemble symmetric α-linked bipyrroles. Among the few methods for preparing unsymmetrical bipyrroles,[22] such as the reaction of donor−acceptor cyclopropanes with 2-cyanopyrroles,[26] the synthesis of 4-alkoxy- and 4-amino-2,2′-bipyrroles from hydroxyproline provides less common products that possess electron-donating substituents.[27] The acylation of the 4-methoxy-2,2′-bipyrrole **1** was explored to study captodative effects on radicals from the comonomer.

4-Methoxy-2,2′-bipyrrole **1** and its sulfonamide **2** were both prepared from hydroxyproline as described.[27,29] 4-Methoxy-5,5′-bistrichloroacetyl-2,2′-bipyrrole (**3**) was synthesized by a double acylation of **1** using trichloroacetyl chloride in diethyl ether (Scheme 1).[28] After 15 min, TLC analysis showed complete consumption of starting material and the formation of monoacylated bipyrrole (R_f = 0.6, hexane/ethyl acetate, 3:1), which underwent the second acylation more slowly. After 2 h, the reaction mixture was quenched and purified by column chromatography to afford dione **3** as a yellow solid in 60% yield. Dimethyl ester **4** was synthesized by treating dione **3** in a haloform reaction with sodium methoxide in methanol in 90% yield after column chromatography on silica gel.

Electrochemistry

Comonomers **1**−**4** all underwent both oxidation and reduction processes (Figure 1) demonstrating their n- and p-type behavior. One discrete reduction process corresponding to the formation of the radical anion was observed in all cases. Similarly, the oxidation process was also a one-electron process resulting in the radical cation. Only a single one-electron transfer process was observed with dione **3** and diester **4** as a result of their high E_{pa} and the limited oxidation window of the solvent. On the other hand, a second one-electron process corresponding to formation of the dication was observed for 4-methoxy-2,2′-bipyrrole **1** and its sulfonamide **2**. In all cases, the observed electrochemical processes were pseudoreversible demonstrating the reactivity of the produced intermediates, which is not surprising in light of unsubstituted terminal positions susceptible to cross-coupling and polymerization by way of radical cation intermediates.

SCHEME 1. **Synthesis of Bipyrroles 3 and 4**



The methoxy group lowered the oxidation potential as seen by the 150 mV decrease in E_{pa} of **1** compared the parent heterocycle, 2,2′-bipyrrole (Table 1).[30−32] This effect is further evident by comparing **4** to its methoxy-free analogue **6**. The introduction of electron-acceptor groups gave more positive E_{pa} values as a result of the electronic push−pull effect. The most pronounced effect was exhibited by dione **3** possessing three times greater E_{pa} than 4-methoxy-2,2′-bipyrrole (**1**). Tuning of the E_{pa} of bipyrroles has thus been demonstrated.

The HOMO and LUMO values were calculated from the measured oxidation and reduction potentials, respectively, according to standard means (Table 1).[33] The E_g was calculated from these values and illustrated the HOMO to be affected more by the electronic groups than the LUMO. The collective affect of the HOMO and LUMO resulted in an energy gap energy variation of 1 eV, while the bipyrroles **1**−**4** are air stable.

The electrochromic properties of the bipyrroles were of particular interest for assessing the effect of the electronic groups on the color of the radical cation. The anodically produced radical cation was spectroscopically characterized when produced by applying a potential to the neutral bipyrrole (Figure 2). Two new absorptions occurred upon electrochemical oxidation of methoxybipyrrole **1**. The isosbestic point at 310 nm confirmed that only two species were present: the neutral form and radical cation. In all cases, the radical cation absorbed at longer wavelengths than the corresponding neutral form. Both the absorptions of the transients of **1** and **3** are bathochromically shifted by only 50 nm. This implied that the HOMO of the radical cation was only slightly increased compared to that of the neutral form. Conversely, the intermediates from **2** and **4** were considerably more stable than their corresponding neutral form as evidenced by their 130 nm bathochromic

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TABLE 1. Electrochemical Data of Bipyrroles Measured in Anhydrous and Deaerated Dichloromethane

compd	λ_{abs}(nm)	λ_{fl} (nm)	Φ_{fl}	λ_{TT}(nm)^a	$E_{pa}{}^1$ (mV)	$E_{pa}{}^2$ (mV)	E_{pc} (mV)	HOMO^b	LUMO^b	E_g	R$^{\bullet+c}$ (nm)
1	291	350	0.01	380	450	1600	−1.4	−4.9	−3.0	1.9	335 (403)
2	260	370	0	380	890	1550	−1.1	−5.3	−3.3	2.0	378 (559)
3	400	420	0.01	450	1350		−1.4	−5.8	−3.0	2.8	380 (591, 342)
4	333	393	0.92	410	980		−1.2	−5.4	−3.2	2.2	380
6[34]	310				1070	1420		−5.5			393 (413, 645)

^{a}Measured in acetonitrile. ^{b}Relative to the vacuum level. ^{c}Refers to the radical cation absorption obtained by applying a potential equivalent to $E_{pa}{}^1$.

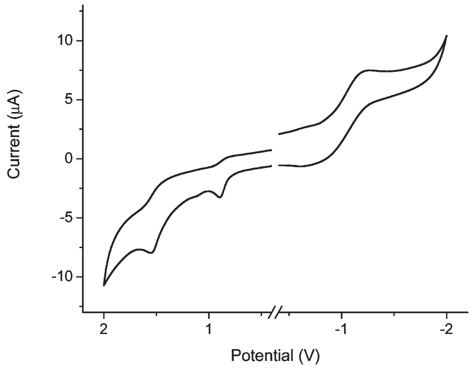

FIGURE 1. Cyclic voltammogram of **2** recorded in deaerated and anhydrous dichloromethane with 0.1 M TBAPF$_6$ supporting electrolyte at a sweep rate of 100 mV/s.

shifts. The data confirmed that color tuning of the electrochemically induced transient was possible.

Spectroscopy

The absorption and fluorescence of the new bipyrroles were investigated further by examining the effect of the electronic groups on the spectroscopic properties (summarized in Table 1). Significant absorption and fluorescence bathochromic shifts resulted from energy gap narrowing and intramolecular electronic effects, as evidenced by the absorbance at 580 nm of **1**, which occurred only in polar solvents versus an absorption at 260 nm in less polar solvents (see Supporting Information). Similarly, dione **3** exhibited solvent dependent absorption. The negative solvatochromism (Figure 3) implies that the ground state of **3** is highly polar as a result of efficient electron push−pull effect.

Except for diester **4**, which fluoresces strongly ($\Phi_{fl} > 0.9$), contingent somewhat on solvent polarity, the bipyrroles did not exhibit fluorescence regardless of the solvent. When laser flash photolysis was used to determine the cause of the weak fluorescence, the bipyrroles, all exhibited transient absorption spectra (Figure 4). The observed intermediates were assigned to the triplet owing to their first order decay (Inset Figure 4) concomitant signal suppression with the common triplet quencher, 1,3-cyclohexadiene. The stabilization effect of the heterocyclic nitrogen is further evidenced by the observed transients that are bathochromically shifted relative to bithiophene (λ_{TT} = 370 nm).[35]

Unsymmetric bipyrroles **1**−**4** possessing electron-donating and -accepting groups were synthesized and shown to be inherently both p- and n-type materials, with tunable oxidation and reduction potentials across a range of 900 mV.

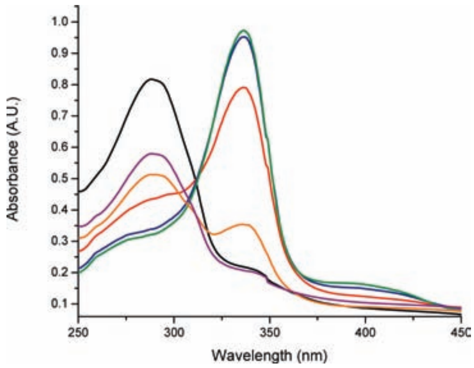

FIGURE 2. Change in absorption of **1** in 0 (black), 1 (red), 5 (blue), and 4 (green) min at a potential of + 850 mV followed by 2.5 (orange), 5 (purple), and 8 (black) min at a potential of −200 mV in anhydrous dichloromethane.

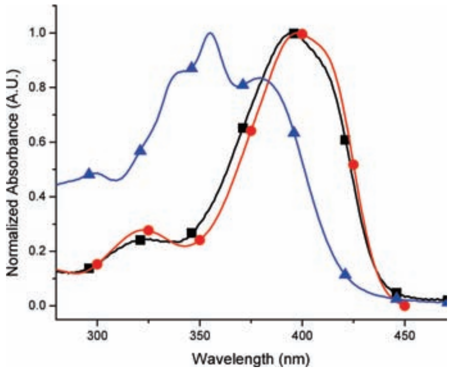

FIGURE 3. Normalized absorption spectra of **3** recorded in acetonitrile (●), dichloromethane (■), and 4:1 methanol/ethanol (▲).

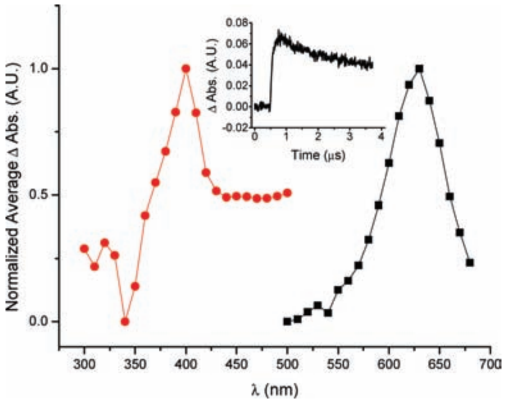

FIGURE 4. Normalized transient absorption spectra of 4 (●) and xanthone reference (■) measured at 1 μs after the laser pulse at 266 nm in deaerated and anhydrous acetonitrile.

Their electrochromic push−pull nature gave significant color changes in the visible spectrum demonstrating that

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bipyrroles are suitable precursors for functional electrochromic materials. The unsymmetric bipyrroles exhibited advantageous properties, including their E_{pa}, the modulation of the absorption of their radical cation with structure, and their tolerance to ambient conditions, properties not readily possible with symmetric bipyrrole and thiophene analogues. Unsymmetric bipyrroles are therefore interesting comonomers for the preparation of electrochromic materials.

Experimental Section

4-Methoxy-5,5′-bistrichloroacetyl-2,2′-bipyrrole (3)[28,36]. Trichloroacetyl chloride (0.6 mL, 5 mmol, 8 equiv) was added to a solution of bipyrrole **2** (105 mg, 0.65 mmol, 100 mol %) in dry diethyl ether (8 mL) under argon at rt. The mixture was stirred at 60 °C for 8 h, diluted with saturated $NaHCO_3$, and extracted with ethyl acetate. The combined organic layer was washed with H_2O and brine, dried with $MgSO_4$, filtered, and concentrated in vacuo to give a yellow solid, which was purified by column chromatography (silica gel, hexane/ethyl acetate, 4:1) to afford dione **3** (174 mg, 60%) as a yellow solid. Mp: 234 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.1 (s, 1H), 9.6 (s, 1H), 7.5 (s, 1H), 6.7 (s, 1H), 6.3 (s, 1H), 4.0 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.5, 172.1, 155.7, 131.3, 130.9, 124.7, 122.7, 112.7, 110.9, 95.9, 95.3, 95.0, 58.7. HR-MS: calcd for $C_{13}H_9Cl_6N_2O_3$ ([M + H$^+$]) 450.8739, found 450.8741.

4-(Methoxy)bismethyl-2,2′-bipyrrole-5,5′-carboxylate (4)[37]. Sodium (0.28 mg, 0.01 mmol, 0.28 equiv) was dissolved in dry methanol (7 mL), and bis-trichloroacetylketone **3** (20 mg, 0.04 mmol, 1 equiv) was added to the reaction mixture, which was stirred at room temperature for 1 h. The volatiles were evaporated, and the resulting solid was dissolved in ethyl acetate (8 mL). The solution was washed with 3 N hydrochloric acid (2 mL) and a saturated sodium hydrogen carbonate solution (2 mL). The organic layer was dried ($MgSO_4$) and concentrated to a residue that was purified by column chromatography (silica gel, hexane/ethyl acetate, 1:1). Evaporation of the collected fractions yielded bipyrrole diester **4** as a brown solid (11 mg) in 90% yield. Mp: 168 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.55 (s, 1H), 10.06 (s, 1H), 6.95 (s,1H), 6.50 (s, 1H), 6.16 (d, J =2.2 Hz, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.89 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.52, 162.5, 154.4, 129.5, 127.7, 123.3, 117.4, 109.0, 107.5, 94.0, 58.6, 52.2, 52.1. HR-MS: calcd for $C_{13}H_{15}N_2O_5$ ([M + H$^+$]) 279.0976, found 279.0983.

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Supporting Information Available: Experimental procedures, characterization data, and NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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